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**Notes:**

1. Untranslatable words are replaced with asterisks (\* \*\*).
2. Texts in the figures are not translated and shown as it is.

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Dictionary: Last updated 04/11/2008 / Priority: 1. Chemistry / 2. JIS (Japan Industrial Standards) term / 3. Technical term

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**CLAIM + DETAILED DESCRIPTION**

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**[Claim(s)]**

[Claim 1] The transparent moisture-proof gas barrier film which carries out spreading membrane formation of the silica sol liquid which comes to an alkoxysilane compound and this alkoxysilane compound on the transparent resin film of a base material considering 5 to 30weight % of a hydrophilic resin composition thing as a principal component, and is characterized by things.

[Claim 2] The transparent moisture-proof gas barrier film according to claim 1 with which a hydrophilic resin composition thing is characterized by being 5 to 30weight % of polyvinyl pyrrolidone to an alkoxysilane compound.

[Claim 3] The transparent moisture-proof gas barrier film according to claim 1 with which a hydrophilic resin composition thing is characterized by being 10 to 30weight % of polyethylene glycol to an alkoxysilane compound.

[Claim 4] Three are [ Claim 1 characterized by an alkoxysilane compound being a mixture of 3 organic-functions alkoxysilane compound and 4 organic-functions alkoxysilane compound - ] the transparent moisture-proof gas barrier film of any one description.

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention relates to films for a package, such as food, drugs, and electronic parts, and relates to the film for a transparent moisture-proof gas barrier property package holding the gas barrier property which was excellent also in the bottom of high humidity especially.

**[0002]**

[Description of the Prior Art] Although that poly vinylidene chloride or polyvinyl chloride carried

out [ that ] resin coating is used for one side or both sides of a transparent resin film general-purpose as a gas barrier property film, Since becoming a cause of a dioxin generation at the time of incineration is pointed out and it becomes the large material of an environmental impact, from home use to business use, these resin is used as a general-purpose packaging film used broadly, and is hot.

[0003] Although the film which coated the transparent resin film with gas barrier property resin, such as polyvinyl alcohol (PVA) and ethylene vinyl alcohol (EVOH), is used instead of this, Since these [ PVA ] and EVOH resin were hydrophilicity, the moisture resistance of the paint film was low, and there was a problem that gas barrier property fell under high humidity.

[0004] Although the film which vapor-deposited ceramic films, such as silica and alumina, to the transparent resin film is used for the package of electronic parts etc. as a film with higher gas barrier property, Vacuum devices expensive for manufacture were needed, since it was the batch production which requires prolonged vacuum suction for every film roll, productivity became what has low and high cost, and this film did not fit a general-purpose packaging film.

[0005] Ceramic film By the applying method, using the sol gel process which is the method of forming membranes inexpensive on a transparent resin film The gas barrier film in which the film which carried out the hybrid of silica membrane, silica, and the gas barrier property resin, such as above PVA and EVOH, was formed is also reported (JP,4-345841,A, JP,8-99390,A, etc.).

[0006] However, there was a problem of producing a crack, without the ability following in footsteps of plasticity of a base film since the silica membrane itself is hard in the case of a silica membrane simple substance, or being hard to obtain sufficient gas barrier property by the detailed opening since the silica membrane by a sol gel process is originally porosity.

[0007] Moreover, in the method of forming the hybrid film of silica and gas barrier property resin, such as PVA and EVOH, since the gas barrier property resin simple substance cannot dissolve in the alcohol which is the solvent of silica sol liquid easily, it is mixed by silica sol liquid in the form of an aqueous solution. as a result -- the quantity of the water in silica sol liquid increases considerably -- sol -- a gel reaction advances rapidly and gels -- being easy -- there was a problem that transparency was easy to be spoiled that it is hard to obtain a homogeneous hybrid film.

[0008] Moreover, it is mixing 3 organic-functions alkoxysilane compound suitable as a silica hybrid film by a sol-gel method apart from this for 4 organic-functions alkoxysilane compound used as a silica raw material, Although there is a report (Journal of the Ceramic Society of Japan, 107 [3], and 293-296) (1999) from which gas barrier property is obtained, reference is not made about the gas barrier property under high humidity conditions.

[0009]

[Problem(s) to be Solved by the Invention] This invention is the transparent gas barrier film

which formed the silica hybrid film by a sol-gel method to the transparent resin film, and is covered to a flexible film base material. The transparent moisture-proof gas barrier film which can maintain gas barrier property also under high humidity conditions is offered without producing a crack on a film.

[0010]

[Means for Solving the Problem] This invention relates to the transparent moisture-proof gas barrier film of the following clauses 1-4.

Clause 1. Transparent moisture-proof gas barrier film which carries out spreading membrane formation of the silica sol liquid which comes to an alkoxysilane compound and this alkoxysilane compound on the transparent resin film of a base material considering 5 to 30weight % of a hydrophilic resin composition thing as a principal component, and is characterized by things.

Clause 2. Transparent moisture-proof gas barrier film given in the clause 1 to which a hydrophilic resin composition thing is characterized by being 5 to 30weight % of polyvinyl pyrrolidone to an alkoxysilane compound.

Clause 3. Transparent moisture-proof gas barrier film given in the clause 1 to which a hydrophilic resin composition thing is characterized by being 10 to 30weight % of polyethylene glycol to an alkoxysilane compound.

Clause 4. Transparent moisture-proof gas barrier film of any one description of the clause 1-3 characterized by an alkoxysilane compound being a mixture of 3 organic-functions alkoxysilane compound and 4 organic-functions alkoxysilane compound.

[0011]

[Embodiment of the Invention] The thing of four organic functions expressed in general formula  $\text{Si}(\text{OR}1)_4$  ( $\text{R}1$  is the alkyl group of carbon numbers 1-5) as the alkoxysilane compound of this invention, Specifically Tetra-ethoxy silane, tetramethoxy silane, tetra-propoxysilane, etc., general formula  $\text{R}2\text{Si}(\text{OR}1)_3$  ( $\text{R}2$  -- aryl groups, such as a phenyl group, --) Organic groups, such as an alkyl group of carbon numbers 1-5 and a vinyl group, and  $\text{R}3$  are organotrialkoxysilane of three organic functions expressed with the alkyl group of carbon numbers 1-5. Specifically Phenyltriethoxysilane, methyl triethoxysilane, They are ethyltriethoxysilane, vinyltriethoxysilane, phenyltrimethoxysilane, methyl trimethoxysilane, ethyltrimethoxysilane, vinyltrimethoxysilane, isopropyl trimethoxy silane, etc. It is combination with tetra-ethoxy silane and phenyltriethoxysilane preferably.

[0012] while an organic ingredient remains into a film and membranous plasticity increases by mixing 3 organic-functions alkoxysilane compound to 4 organic-functions alkoxysilane compound -- sol -- it can be made hard to ease contraction of the film by a gel reaction and to happen in a membranous crack. When adding 3 organic-functions alkoxysilane compound, it is desirable that the ratio of four organic functions and three organic functions is about 8:2 in a

bulk density. On the contrary, when there is too much quantity of 3 organic-functions alkoxy silane compound, it becomes difficult to dry at the time of membrane formation, and there is also a problem that stickiness remains in a film easily.

[0013] The hydrophilic resin composition thing of this invention serves to control the volumetric shrinkage to be the resin composition thing which has the functional group which carries out a hydrogen bond to the silanol group which an alkoxy silane compound hydrolyzes and produces, and according to the polycondensation of silanol groups by the reaction, and to prevent a membranous crack. [ the functional group which carries out a hydrogen bond to a silanol group has a hydroxyl group, a carbonyl group, an amide group, an urea machine, a urethane group, an imido machine, etc., and / a suitable resin composition thing ] Specifically, there are polyethylene glycol, polyvinyl pyrrolidone, poly oxazoline, Pori N, N-dimethyl acrylamide, polyalkylene glycol methacrylate, polyalkylene glycol acrylate, etc. They are polyethylene glycol and polyvinyl pyrrolidone preferably.

[0014] Moreover, polyethylene glycol methacrylate, polyethylene glycol acrylate, etc. which esterified the end of polyethylene glycol with acrylic acid can be used, and membranous moisture resistance can be raised by carrying out ultraviolet radiation bridge formation according to concomitant use of a photopolymerization initiator in that case.

[0015] The amount of addition of a hydrophilic resin composition thing has 5 to 30weight % of a desirable range to an alkoxy silane compound, and is 10 to 20weight % of a range more preferably. If there are few amounts of addition of a hydrophilic resin composition thing than 5 weight %, it will become easy to generate a crack after membrane formation, and if there are more amounts of addition conversely than 30 weight %, a paint film will become thick too much and will become easy to produce a crease on a film.

[0016] The molecular weight of a hydrophilic resin composition thing has a respectively suitable range, and if it is polyvinyl pyrrolidone and it is 630000-40000, and polyethylene glycol, its range of 1000-100 is desirable. If the molecular weight of a hydrophilic resin composition thing is large -- sol -- being hard to dissolve at the time of mixing to liquid, and dissociating -- being easy -- the effect of addition will become small if molecular weight is conversely small.

[0017] The water and the acid catalyst for carrying out an alcohol solvent and hydrolysis reaction other than the above-mentioned alkoxy silane compound are required for the silica sol liquid of this invention.

[0018] There are ethanol, methanol, isopropyl alcohol, etc. as an alcohol solvent. To 1mol of the above-mentioned alkoxy silane compounds, if it is 5-50mol and there are many amounts of solvents, a film will become thin, a gas barrier function will fall, conversely, if there are few amounts of solvents, thickness will become thick and, as for the quantity of an alcohol solvent, a crack will go into a film easily.

[0019] As an acid for acid catalysts, hydrochloric acid, nitric acid, sulfuric acid, acetic acid, etc. can be used. It is about 0.005-0.1mol, to 1mol of the above-mentioned alkoxysilane compounds, if there is more quantity than this, hydrolysis reaction velocity will become quick, membranous surface nature worsens, if there is little quantity conversely, a rate of reaction will become slow and, as for the quantity of an acid, membrane formation time will become long.

[0020] Moreover, if a film will porosity-ize, precise nature will be lost to 1mol of the above-mentioned alkoxysilane compounds, if it is about 1-10mol and there is more quantity than this, and the quantity of water has little quantity conversely, a rate of reaction will become slow or an unreacted thing will remain easily. Here, when both 3 organic-functions alkoxysilane compound and 4 organic-functions alkoxysilane compound are used, the above-mentioned thing is applied to 1mol of the total amount.

[0021] [ the transparent resin film of the base material used for this invention ] If it is the extrusion of transparent resin and the cast shaping \*\*\*\* film which have the heat-resisting property of about 100 degrees C, are [ anything ] good. There are polyethylene, polypropylene, polyethylene terephthalate, polycarbonate, polyether sulphone, polysulfone, cyclic polyolefin, Pori methyl pentene, nylon, etc., and it is properly used according to the purpose of use or cost. 5-100 micrometers of thickness of a transparent resin film is 10-30 micrometers preferably. 80 to 93%, the permeability of a transparent resin film is about 91% preferably, and is making the barrier coat of this invention this, and permeability improves to about 92% preferably 83 to 95%. This is because the surface smoothness of a film becomes good on a barrier coat and optical diffusion in the surface is reduced.

[0022] The general spreading methods, such as dipping, a spray, a spin coat, a roll coat, and a photogravure coat, can be used for the spreading membrane formation method of this invention. The range of thickness of 0.2-10 micrometers is desirable, and it is 1-3 micrometers more preferably.

[0023] neglecting several minutes - about one evening in a room temperature after spreading - after that -- preferably, still more preferably, at the temperature of about 100 degrees C, it dries for several 10 minutes - several hours or more, and 80-120 degrees C 50-150-degree C form membranes. If a drying temperature is made high within the limits of the heat-resisting property of a base film, it can dry more in a short time.

[0024] It is thought that discovery of the high gas barrier property by the silica hybrid film of this invention is based on the following Reasons. Although the silica membrane by a sol-gel method is a film with many openings [ porosity originally ] sol - [ with the acid in liquid (it is 0.005-0.015mol to 1mol of alkoxysilane compounds), and control of a moisture content (it is 1-6mol to 1mol of alkoxysilane compounds) ] Also by carrying out the hydrogen bond of the hydrophilic resin composition thing with precise membrane formation possible by not three dimensions but 1, and making it go on in two dimensions in the reaction of silica, and the still

more suitable above to a silanol group, and lessening the reactive site of a silanol group Since a silica reaction can be controlled more nearly superficially, it is thought that a more precise film is formed. [ a moisture child staying all over a hole and preventing passage of gas molecules, such as nitrogen and oxygen, since a film is hydrophilicity if a steam permeates all over a detailed hole in such fine porous membrane ] It is reported by porous glass and it is thought that the high gas barrier property under high humidity is discovered with such an operation also in this film.

[0025]

[Example] Below, it explains in full detail further according to a work example with a comparative example.

[0026] (Work example 1) Tetra-ethoxy silane, ethanol, distilled water, and nitric acid were mixed at a rate of the molar ratio 1:20:2:0.01, it agitated for 3 hours, and silica sol liquid was obtained. To this, addition mixing of 5, 10, and 20 or 30weight % of the polyvinyl pyrrolidone (molecular weight 360000) was carried out, respectively, it agitated to the weight of tetra-ethoxy silane, for 2 hours, and each hydrosol liquid for gas barrier coating was obtained to it.

[0027] After carrying out the spin coat (number of rotations of 1000rpm, time 20 seconds) of the above-mentioned coating liquid and neglecting it in a room temperature overnight on the nylon integral multi-pack film (Gunze HEPUTAKKUSU and 15 micrometers in thickness) which is the lamination of nylon / EVOH / nylon, it was made to dry in 100-degree C oven for 8 hours.

[0028] About the gas barrier property of the created film, Mocon OX-TRAN 200H was used and oxygen permeability was evaluated by the method of JIS-K7126. Measurement was performed on condition of 20-degree-C80% RH. The result is shown in Table 1.

[0029]

[Table 1]

ポリビニルピロリドン添加量 (w t %)	膜厚 ( $\mu$ m)	酸素透過率 (cc/m <sup>2</sup> /day)
5	2.2	3.9
10	2.0	0.1
20	3.7	2.0
30	11.0	2.7

Although the oxygen permeability of a nylon integral multi-pack film without coating is below 2 cc/m<sup>2</sup>/day under ordinary temperature usual state humidity, Although it will increase to 28.3 cc/m<sup>2</sup>/day and gas barrier property will fall under 20-degree-C80% RH of high humidity, the gas barrier property under high humidity improved sharply by the above-mentioned gas barrier coating.

[0030] (Work example 2) Silica sol liquid was produced like the work example 1. To this, to the weight of tetra-ethoxy silane, mixed churning of 10 and 20 or 30weight % of the polyvinyl

pyrrolidone (molecular weight 630000) was carried out like the work example 1, and each hydrosol liquid for gas barrier coating was obtained, respectively.

[0031] After carrying out the spin coat (number of rotations of 1000rpm, time 20 seconds) of the above-mentioned coating liquid and neglecting it in a room temperature overnight on a nylon integral multi-pack film (Gunze HEPUTAKKUSU and 15 micrometers in thickness), it was made to dry in 100-degree C oven for 8 hours.

[0032] The gas barrier property of the created film was measured like the work example 1. The result is shown in Table 2.

[0033]

[Table 2]

ポリビニルピロリドン添加量 (w t %)	膜厚 ( $\mu$ m)	酸素透過率 (cc/m <sup>2</sup> /day)
10	2.0	9.2
20	3.0	4.4
30	10.2	1.3

The gas barrier property under high humidity improved sharply like the work example 1.

[0034] (Work example 3) Tetra-ethoxy silane, ethanol, distilled water, and hydrochloric acid were mixed at a rate of the molar ratio 1:5:2:0.01, it agitated for 3 hours, and silica sol liquid was obtained. To the weight of tetra-ethoxy silane, to this, 30weight % of polyethylene glycol (molecular weight 600) was mixed, it agitated to it for 2 hours, and the hydrosol liquid for gas barrier coating was obtained to it.

[0035] After carrying out the spin coat (number of rotations of 1000rpm, time 20 seconds) of the above-mentioned coating liquid and neglecting it in a room temperature overnight on a nylon integral multi-pack film (Gunze HEPUTAKKUSU and 15 micrometers in thickness), one evening was dried in 100-degree C oven.

[0036] The gas barrier property of the created film was measured like the work example 1.

[0037] Thickness is 2.5 micrometers, oxygen gas permeability is 8.7 cc/m<sup>2</sup>/day, and the gas barrier property under high humidity improved.

[0038] (Work example 4) Tetra-ethoxy silane, phenyltriethoxysilane, ethanol, distilled water, and hydrochloric acid (acid catalyst) were respectively mixed at a rate of 0.8:0.2:5:4:0.01 by the molar ratio, it agitated for 3 hours, and hydrosol liquid was obtained. To the total weight of tetra-ethoxy silane and phenyltriethoxysilane, 30 weight % of polyethylene glycol of molecular weight 600 was mixed to this, it agitated to it for 2 hours, and the hydrosol liquid for gas barrier coating was adjusted to it.

[0039] After carrying out spin coat (number-of-rotations [ of 1000rpm ], time 20 seconds) spreading of the above-mentioned coating liquid and neglecting one evening at a room temperature on a nylon integral multi-pack film (15 micrometers in thickness, Gunze HEPUTAKKUSU), one evening was dried in 100-degree C oven.

[0040] The gas barrier property of the created film was measured like the work example 1.

[0041] Thickness is 2.2 micrometers, oxygen gas permeability is 2.6 cc/m<sup>2</sup>/day, and the gas barrier property under high humidity improved sharply.

[0042] (Comparative example 1) The ratio of the polyethylene glycol (molecular weight 600) to add was carried out to 50weight % like the work example 3, and the hydrosol liquid for gas barrier coating was obtained.

[0043] After carrying out the spin coat (number of rotations of 1000rpm, time 20 seconds) of the above-mentioned coating liquid and neglecting it in a room temperature overnight on a nylon integral multi-pack film (Gunze HEPUTAKKUSU and 15 micrometers in thickness), one evening was dried in 100-degree C oven.

[0044] The gas barrier property of the created film was measured like the work example 1.

[0045] Although thickness is 2.7 micrometers, oxygen gas permeability is 15.6 cc/m<sup>2</sup>/day and the gas barrier property under high humidity was discovered, compared with the work example 3, it became low.

[0046] (Comparative example 2) Except that the rate of the polyvinyl pyrrolidone (molecular weight 360000) to add was 40 weight %, the hydrosol liquid for gas barrier coating was produced like the work example 1.

[0047] After carrying out the spin coat (number of rotations of 1000rpm, time 20 seconds) of the above-mentioned coating liquid and neglecting it in a room temperature overnight on a nylon integral multi-pack film (Gunze HEPUTAKKUSU and 15 micrometers in thickness), one evening was dried in 100-degree C oven.

[0048] Since membranous thickness was thick, the crease occurred over the whole film surface after desiccation by membranous contraction, and it changed into the state where it cannot be used as a packaging film.

[0049] (Comparative example 3) The rate of the polyvinyl pyrrolidone (molecular weight 360000) to add was carried out to 1weight % like the work example 1, and the hydrosol liquid for gas barrier coating was produced. After carrying out the spin coat (number of rotations of 1000rpm, time 20 seconds) of the above-mentioned coating liquid and neglecting it in a room temperature overnight on a nylon integral multi-pack film (Gunze HEPUTAKKUSU and 15 micrometers in thickness), one evening was dried in 100-degree C oven. The gas barrier property of the created film was measured like the work example 1.

[0050] Thickness is 1.1 micrometers, oxygen gas permeability is 18.7 cc/m<sup>2</sup>/day, and the gas barrier property under high humidity became low compared with the work example 1.

[0051] (Comparative example 4) The ratio of the polyethylene glycol (molecular weight 600) to add was carried out to 5weight % like the work example 3, and the hydrosol liquid for gas barrier coating was obtained.

[0052] After carrying out the spin coat (number of rotations of 1000rpm, time 20 seconds) of



the above-mentioned coating liquid and neglecting it in a room temperature overnight on a nylon integral multi-pack film (Gunze HEPUTAKKUSU and 15 micrometers in thickness), one evening was dried in 100-degree C oven.

[0053] The crack was observed by the obtained film with the magnifying glass, and gas barrier property was not obtained.

[0054]

[Effect of the Invention] By coating the silica membrane which mixed the specific hydrophilic resin composition thing by the sol gel process on a transparent resin film, gas barrier property cannot fall under high humidity, but a transparent gas barrier film suitable for food packing etc. can be obtained.

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[Translation done.]